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Response to thermal exposure of the mechanically alloyed Al–Ti/C powders

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Abstract Al–TiC$_p$ composites have been extensively studied in recent years not only because of their attributes as wear-resistant structural materials but also on account of their potential as very efficient grain refiners. Al–Ti–C alloys of various compositions have already been commercialized as grain refining master alloys and have long been in use in aluminium foundries world wide. The present work was undertaken to investigate the possibility of manufacturing Al–TiC$_p$ grain refiner master alloy tablets by the mechanical alloying route. Carbon was mechanically alloyed into Al–Ti alloy powder grains via high energy ball milling. The Al–Ti/C powder blend thus obtained was heat treated to promote the precipitation of TiC. Al_4C_3 was the first phase to form inside the powder grains upon thermal exposure. The Al_4C_3 particles which were too small to be identified with the optical microscope until 750 °C, have grown until 850 °C where they have started to react with Al_3Ti to produce TiC. A very fine dispersion of TiC particles was thus generated inside the powder particles while the Al_3Ti phase has almost vanished.

Introduction

Al–TiC$_p$ composites combine the ductility and toughness of the aluminium matrix with the strength, stiffness, hardness and wear resistance of TiC particles, leading to a unique combination of properties [1]. Al–TiC$_p$ composites are attractive candidates for various structural applications, particularly in the automotive sector, as they offer favorable mechanical properties in addition to substantial weight savings. They have been extensively studied in recent years not only because of their attributes as wear-resistant structural materials but also on account of their potential as very efficient grain refiners [2–7]. Al–Ti–C alloys of various compositions have already been commercialized as grain refining master alloys and have long been in use in aluminium foundries world wide [4, 8].

Al–TiC$_p$ composites can be obtained by adding TiC powders directly into the melt, often by mechanical means [2] and by in situ reactions between Al–Ti melts and various carbon sources [3, 9–13]. The direct introduction of TiC powder into the melt has difficulties, as TiC particles are hardly wet by aluminium melts unless a suitable flux is used to aid the incorporation process [14]. In addition, the TiC particles are not in thermodynamic equilibrium with molten aluminium, and thus react with the matrix leading to a poor interface and substantial degradation in properties [9]. These problems are largely overcome by the in situ formation of TiC particles in aluminium melts [15]. Since the in situ formed TiC particles are thermodynamically stable, the matrix–particle interfaces tend to be clean, free from adsorbed gases, oxide films and detrimental reaction products and are thus much stronger.

Some in situ techniques to synthesize Al–TiC$_p$ composites involve Powder Metallurgy (PM) methods [16, 17]. PM-processed composites are superior to their cast counterparts which suffer poor mechanical properties due to the clustering of reinforcing particles during solidification processing [14]. PM processing often involves sintering of powder blends prepared by mechanical milling/alloying of individual elements. Mechanical alloying, as a method of introducing the reinforcement particles, assures better dis-

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tribution of the particles in the consolidated material [18, 19]. In the present work, carbon was mechanically alloyed with Al–5Ti alloy powder via high energy ball milling and carbide particles were precipitated during subsequent heat treatment. Preliminary results of an ongoing work aimed at manufacturing Al–TiC_p grain refiner master alloy tablets by cold pressing the powder blends thus produced, will be briefly outlined.

Experimental

A mix of 5 g Al–5Ti (wt%) alloy powder (maximum particle size: 350 microns), obtained by mechanically pulverizing an Al–5Ti master alloy ingot, and 0.5 g graphite powder was dry-milled using a Spex 8000 laboratory mill using hardened steel vial and steel balls. Some Al–5Ti/C powder blends were spex-milled only several minutes to achieve mixing, and other Al–5Ti/C powder blends were milled for up to 6 h to incorporate carbon into the Al–5Ti particles. The milled powders were heated in the differential thermal analyzer (DTA) cell until 1,000 °C to investigate their response to thermal exposure. The DTA experiments were performed under flowing argon at a heating rate of 20 °C/min. Larger volumes of Al–5Ti/C powder blends were heat treated in a tube furnace in the same manner as that employed in the DTA experiment, to temperatures which mark the end of the major thermal signals displayed in the DTA curve. They were then quenched to room temperature to limit further transformation. The heat treated powder blends were subsequently analyzed with X-ray diffraction (XRD) and metallographic techniques, in order to identify the compounds and determine the reactions responsible for the DTA signals. XRD was conducted with CuK_α radiation at a scan rate of 0.5°/min in order to improve the counting frequency. Samples for metallographic analysis were prepared using conventional practices and were examined with optical and scanning electron microscopes. Measures were taken during metallographic sample preparation to avoid a possible reaction between water and any Al_4C_3 that may be present in the heated samples.

Results and discussion

The starting Al–5Ti powder grains were found by XRD analysis to contain blocky Al_3Ti particles of various sizes (up to about 20 microns) dispersed in an aluminium matrix (Fig. 1a). During high-energy ball milling, the powder particles are subjected to repetitive deformation, fracture and welding events when trapped between colliding balls. High-energy ball milling morphologies are evident from the optical micrographs of the Al–5Ti/C powder blends sampled in the course of milling operation. A layered structure typical of the initial stages of milled powder blends has formed after 15 min of milling. This layered structure has become refined, with increasing milling time to 3 h (Fig. 1b). After 6 h of milling, a more homogeneous mixture of Al and C with a generally very fine dispersion of Al_3Ti intermetallic particles has developed (Fig. 1c). Although some blocky Al_3Ti particles are still present in the powders, most Al_3Ti particles have fractured and deformed significantly during milling and could hardly be resolved in the majority of the powder grains. Some solutionizing of Ti

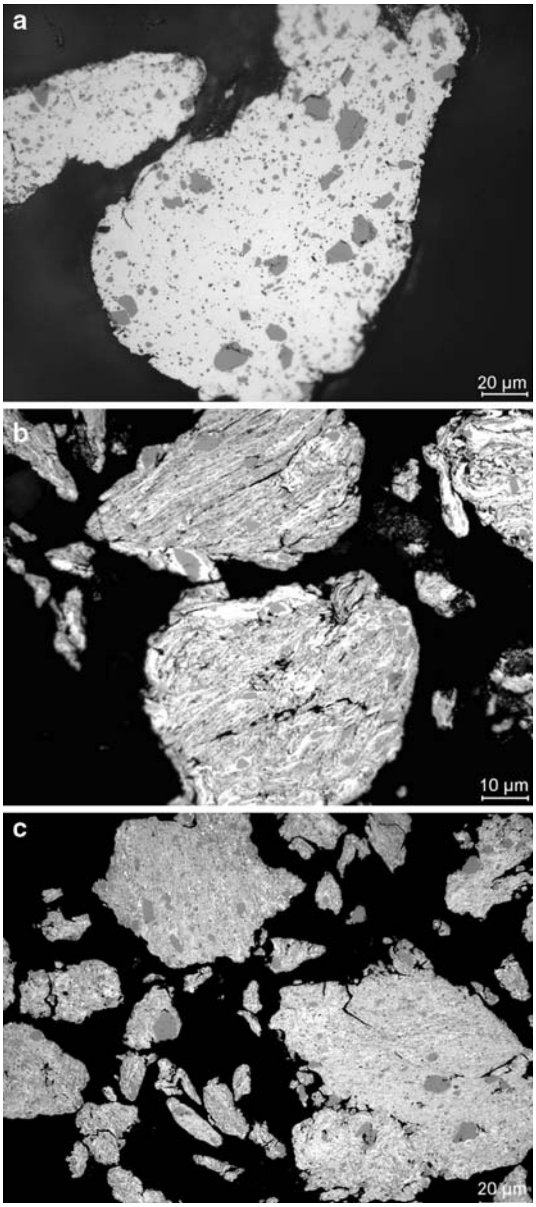

Fig. 1 The optical micrographs of (**a**) the ground Al–Ti alloy powder, of the Al–5Ti/C powder blends submitted to high energy ball milling for (**b**) 3, (**c**) 6 h

in the aluminium matrix is also believed to have taken place. Lattice parameter calculations using the Nelson–Riley extrapolation function has shown that the lattice parameter of the 6-h milled sample was 0.0045 Å smaller with respect to the starting powder blend. This is made possible by the propensity mechanical alloying has to access many metastable states under circumstances when the Al–Al_3Ti is the stable two phase equilibrium for the powder and when the formation of Al(Ti) extended solid solution would be thermodynamically unfavorable. The deformation introduced by milling and the decrease in crystallite size of the Al_3Ti particles by fragmentation and possibly subgrain formation have all produced a gradual broadening of Al_3Ti reflections in the XRD patterns of the as-milled samples with increasing milling time. No evidence for carbide formation was noted after milling for up to 6 h, either by XRD or optical microscopy.

The DTA scan of the Al–5Ti/C samples, milled for only 5 min, to blend the powders, revealed only a major endothermic trough produced by the melting of the aluminum matrix (Fig. 2a). However, three additional signals developed in the DTA scan of the powder blends milled for 3 and 6 h (Fig. 2b,c). The first two of these signals (peaks 1,2), recorded right before and after the melting of the aluminium matrix, were exothermic peaks while the last signal (signal 3) was an endothermic trough which started at approximately 850 °C. The peak arrangement in Fig. 2b, c seems to imply that the former two have been generated by the same reaction which spreads over a range of temperatures, including that of the melting of the aluminium matrix. The second exothermic peak may develop only after reaction with molten aluminium. The change in their relative intensities suggests that the exothermic reaction responsible for these two peaks is enhanced with increasing milling time. The endothermic trough at 850 °C, on the other hand, seems to be unaffected by the milling history of the sample and has remained at the same temperature.

The XRD pattern of the Al–5Ti/C powder blend after 6 h of milling, exhibits broad Al_3Ti reflections in addition to those of the aluminium matrix (Fig. 3a). It is inferred from the XRD pattern of the as-milled powder blend that the Al_3Ti phase has been refined extensively and that no carbide formation has taken place during the milling process. Broad Al_4C_3 reflections, which were absent in the XRD pattern of the powder blend heated to 550 °C (Fig. 3b), were noted after heating to 620 °C, until after the first exothermic peak (Fig. 3c). This peak is likely primarily caused by the formation of Al_4C_3 from a reaction between aluminium and carbon. The rather weak and broad nature of the Al_4C_3 reflections imply that the amount of carbide formation occuring by 620 °C is limited and that the precipitating Al_4C_3 particles at this stage are very small. The Al_4C_3 particles are indeed too small to be resolved with the optical microscope (Fig. 4a). In the meantime, Al_3Ti reflections have gained some intensity with respect to those in the as-milled state (Fig. 3c), suggesting that some coarsening or strain release of the aluminide particles has taken place during heating to 620 °C, or possibly precipitation of Al_3Ti from the solid solution matrix.

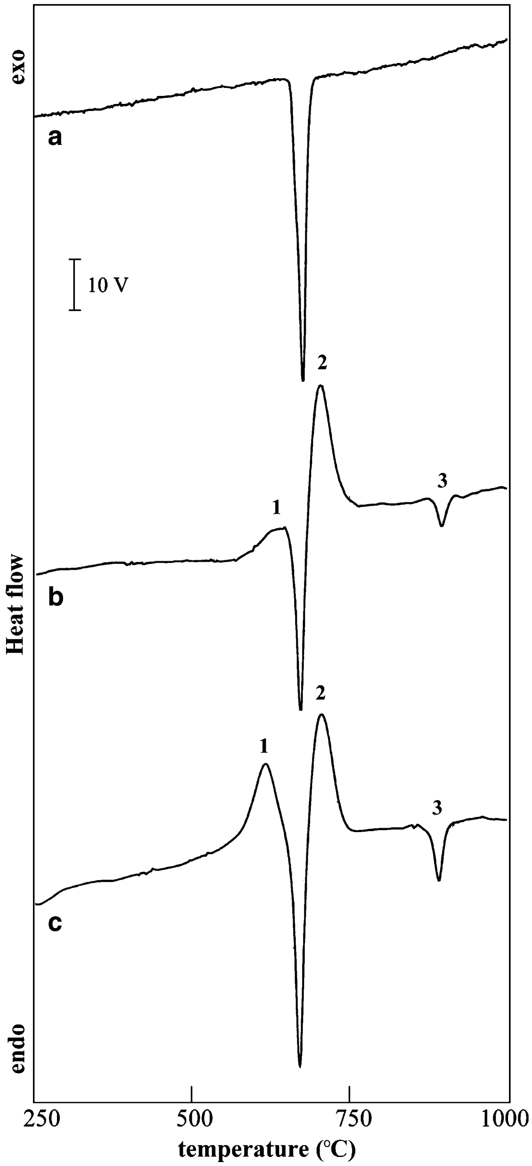

Fig. 2 The DTA thermograms of the Al–5Ti/C powder blends after ball milling for (**a**) 5 min, (**b**) 3 h and (**c**) 6 h

The Al_4C_3 reflections have grown larger and have become sharper after the Al–5Ti/C powder blend milled for 6 h was heated to 750 °C, to the end of the second exothermic signal (Fig. 3d) while there was hardly any change in the Al_3Ti reflections. Further Al_4C_3 formation is thus claimed to be responsible also for the second exothermic peak. This reaction was apparently accelerated once the

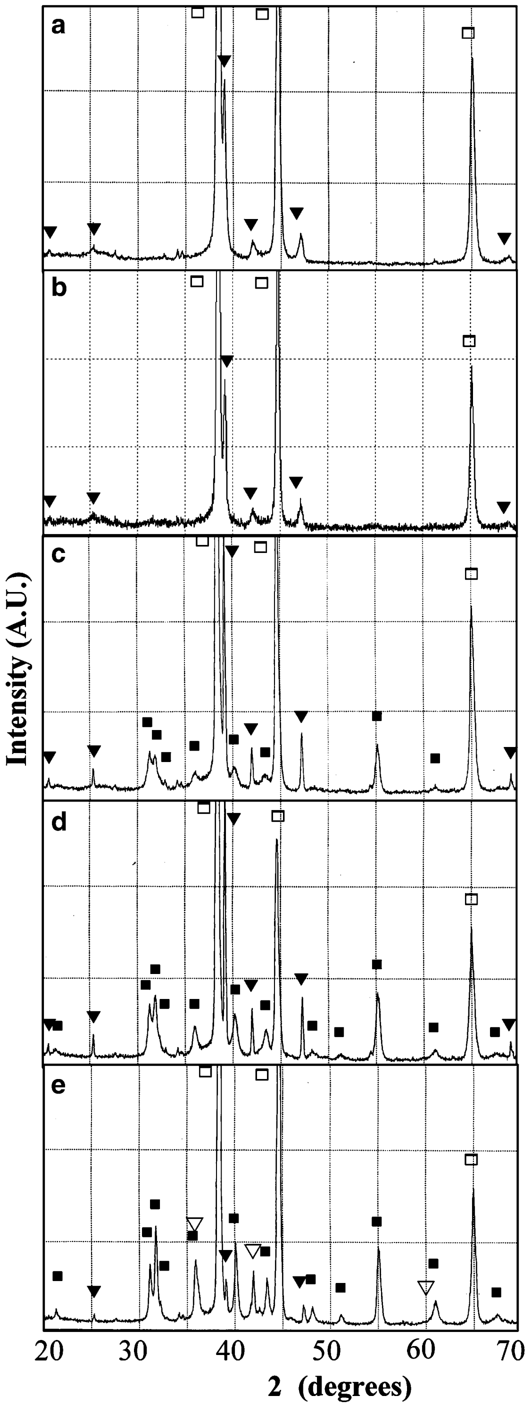

Fig. 3 X-ray diffraction patterns of the Al–5Ti/C powder blends (**a**) submitted to high energy ball milling for 6 h and then heated to (**b**) 550 °C, (**c**) 620 °C, (**d**) 750 °C and (**e**) 900 °C and then quenched (□: Al; ▼: Al3Ti; ■: Al$_4$C$_3$; ▽:TiC)

aluminium matrix has melted owing to the much higher diffusion rates in the liquid state. It appears that peaks 1 and 2 are actually the leading and trailing portions of a wider exothermic peak between 570 °C and 750 °C, where the predominant reaction is the formation of Al$_4$C$_3$. This

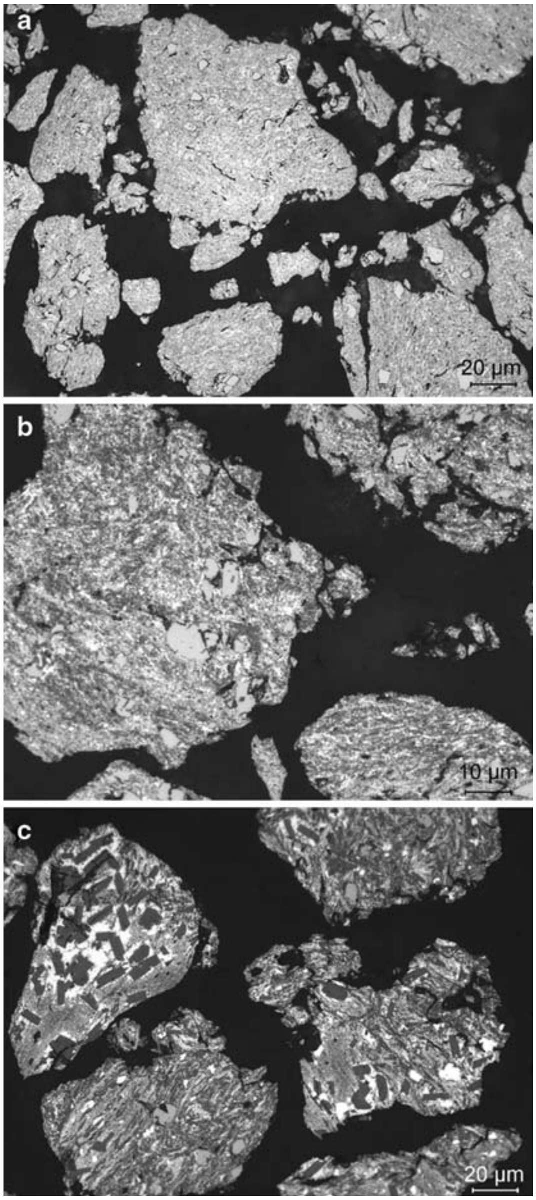

Fig. 4 Optical micrographs of the Al–5Ti/C powder blends submitted to high energy ball milling for 6 h and then heated to (**a**) 620 °C, (**b**) 750 °C and (**c**) 900 °C and then quenched

precipitation reaction is occurring concurrently with the highly endothermic melting activity of the aluminium matrix, generating two exothermic signals interrupted by an endothermic trough. The Al–5Ti/C powder blend heated to 750 °C after 6 h of high energy ball milling has responded to etching and has developed a dark contrast along the very fine mechanically alloyed layers in each powder particle. The very fine dispersion of precipitates observed along these layers, are thus claimed to be of the Al$_4$C$_3$ variety (Fig. 4b). The Al$_3$Ti intermetallic phase is still present after heating to this temperature range as evidenced by the XRD analysis and metallographic investigations.

These observations are in agreement with an earlier investigation, where Al_3Ti and Al_4C_3 were reported to be the only phases in Al–10 wt% TiC composite samples reacted for 48 h, and then held at 700 °C [2].

Major changes were noted in the XRD spectrum of the Al–5Ti/C powder blend milled for 6 h and heated to 900 °C, until after the endothermic trough (reaction 3) and then quenched. The intensity of the Al_3Ti reflections have significantly decreased while reflections of the TiC phase were noted for the first time (Fig. 3e). While the locations of most Bragg reflections of the TiC phase coincides with those of the Al_4C_3 phase, the (200) reflection of the TiC phase at $2\theta = 41.746$, helps to identify this phase conclusively. The XRD pattern indicates that α-Al, Al_4C_3, Al_3Ti and TiC phases coexist in the powder after heating the Al–5Ti/C blend milled for 6 h to 900 °C. The following four phase reaction, i.e.

$$3Al_3Ti + Al_4C_3 \rightarrow 3TiC + 13Al \qquad (1)$$

observed by Nukami and Flemings [20] in a mechanically alloyed powder mixture of Al_3Ti, Al_4C_3 and Al provides a plausible account of the observed microstructural changes. This reaction is endothermic and becomes thermodynamically favorable at approximately 800 °C (Fig. 5). Considering the peak shift that must have taken place at the heating rate employed in the DTA experiments (20 °C/min), the onset of the endothermic signal 3, measured from the DTA scans (850 °C) is judged to be in reasonable agreement with that estimated from thermodynamic data [21] and also with the reaction temperatures reported in earlier investigations [22–28].

Further evidence for Al_4C_3, Al_3Ti and TiC phases in Al–5Ti/C powder blend heated to 900 °C after 6 h high energy ball milling, is shown by metallographic analysis. One can readily identify the coarse, angular Al_4C_3 particles and the relatively smaller blocky Al_3Ti particles (Fig. 4c). The Al_4C_3 particles appear dark while Al_3Ti particles appear gray in the optical micrographs. Some Al_4C_3 particles have apparently undergone substantial coarsening during heating to 900 °C. The fraction of Al_4C_3 particles, smaller in size, has reacted with Al_3Ti in the temperature range of the endothermic trough, to produce the TiC phase. The TiC particles thus produced were very fine and were dispersed in the aluminium matrix (Fig. 6). The majority of the Al_4C_3 particles, however, have survived the above reaction, since the amount of carbon used in the milling experiments was far greater than that required to achieve full conversion of the available Ti into TiC.

These results suggest that carbon must be dispersed into Al–5Ti powder grains for carbide formation reactions to take place. The powder blends milled only for several minutes to obtain a blended mixture reveals no evidence of carbide formation. The mechanically alloyed Al–5Ti/C powder blends after hours of milling, on the other hand, first undergo some Al_4C_3 formation on heating above 600 °C. At temperatures of approximately 850 °C, the Al_3Ti can react with Al_4C_3, or possibly free unreacted carbon to form the TiC phase. The synthesis of Al–TiC_p composites by thermal treatment of the mechanically alloyed Al–5Ti/C powder blends appears to be feasible.

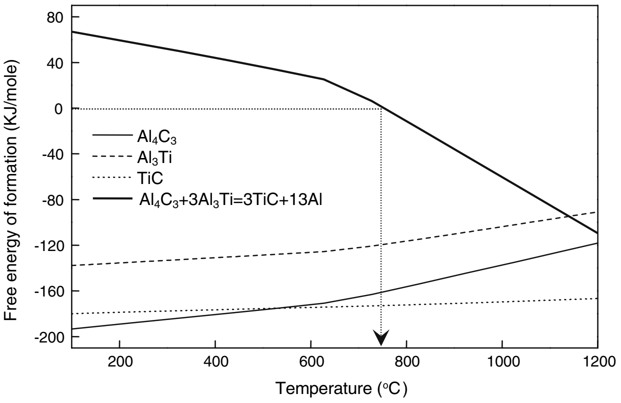

Fig. 5 The free energy of formation for Al_4C_3, Al_3Ti, TiC and the free energy change associated with the four phase reaction: $3Al_3Ti + Al_4C_3 \rightarrow 3TiC + 13Al$

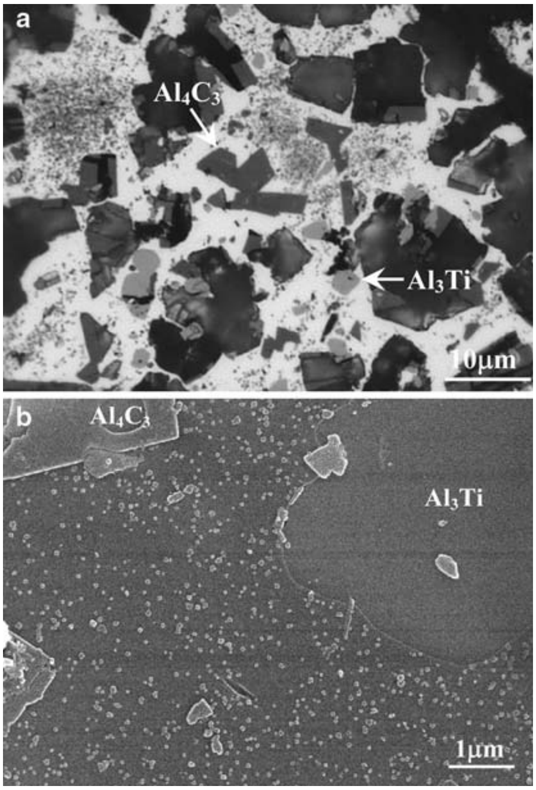

Fig. 6 (**a**) Optical and (**b**) scanning electron micrographs of the Al–5Ti/C powder blends submitted to high energy ball milling for 6 h and then heated to 900 °C and then quenched

The carbon addition has to be carefully adjusted and heat treatment times considered, however, to limit the amount of residual Al_4C_3 in the final composite.

Summary

Al–5Ti alloy powder was mechanically alloyed with carbon using a Spex 8000 laboratory mill. The layered structure typical of mechanically alloyed powders, formed after fairly short milling times (approximately 15 min) was refined by further milling to develop a more or less homogeneous mixture of Al and C and a fine dispersion of Al_3Ti particles. Al_4C_3 was the first phase to form when the Al–5Ti/C powder blend was heated. The formation of Al_4C_3 was accelerated once the aluminium matrix has melted. The amount of Al_4C_3 particles increase until 850 °C where they have begun to react with Al_3Ti to produce TiC according to: $3Al_3Ti + Al_4C_3 \rightarrow 3TiC + 13Al$. A fine dispersion of TiC particles was thus generated inside the powder grains. A notable fraction of the Al_4C_3 particles, however, have survived the above reaction. Al–TiC_p powder can be synthesized by adjusting the C content of the Al–5Ti/C powder blend and temperature and time of the heat treatment after milling. Achievement of a Al–TiC composite would require careful optimization of these parameters to assure the TiC formation reaction can go to completion.

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